

Structural and electronic properties of compressed selenium and tellurium under high pressure

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We investigate the mechanisms of the nonmetal-metal transitions of Se and Te induced by the volume compression both in the solid and liquid states by the density functional method. The volume compression increases the band width and the system transforms from nonmetal to metal phase both in the crystalline Se and Te. When the system has structural disorder, the energy of the anti-bonding level corresponding to long bonds is decreased. This situation induces a nonmetal-to-metal transition in liquid Se under compression at a pressure lower than that for crystalline Se as well as in melting of Te under the normal pressure.

Introduction

Recently, we have proposed a new mechanism for the nonmetal-to-metal transition concerning with the behavior of liquid selenium (l -Se) near the liquid-vapor critical point under high temperature (T) and high pressure (P).¹⁻⁶⁾

Crystalline selenium (c -Se) and tellurium (c -Te) exhibit semiconductor (nonmetal) properties and have trigonal structures, consisting of hexagonal arrays of helical chains of atoms with twofold coordination. When P is increased, c -Se transforms from a nonmetal to a metal at $P = 18$ GPa and so does c -Te at $P = 4$ GPa.⁷⁾

In the liquid state, on the other hand, there are large differences in the electronic properties between Se and Te. Liquid Se is composed of long chains and exhibits a semiconductor-like behavior. It transforms from a semiconductor to a metal at $P = 3$ GPa,⁸⁾ while liquid Te (l -Te) shows a metallic behavior under normal pressure.⁹⁾

The transition pressures from a semiconductor to a metal are different between the solid and liquid states and the elec-

tronic properties of Se and Te are very different in the liquid state.

In this paper, we calculate the band levels of the structural models for these compressed Se and Te by the density functional method with the local density approximation. We investigate the mechanisms of the nonmetal-to-metal transitions of Se and Te induced by the volume compression both in the solid and liquid states.

Models and calculation method

It is known from experimental results that l -Se slightly above the melting temperature has a long chain structure, whose average chain length (n) is estimated to be about 10^5 atoms, with twofold coordination.¹⁰⁻¹²⁾ By taking into account these experimental results, we propose model systems composed of infinite helical chains for compressed Se and Te illustrated in Fig. 1. For the purpose of simulating the essential aspects of structural disorder in liquids, we assume that the bonds on each chain have long and short lengths.

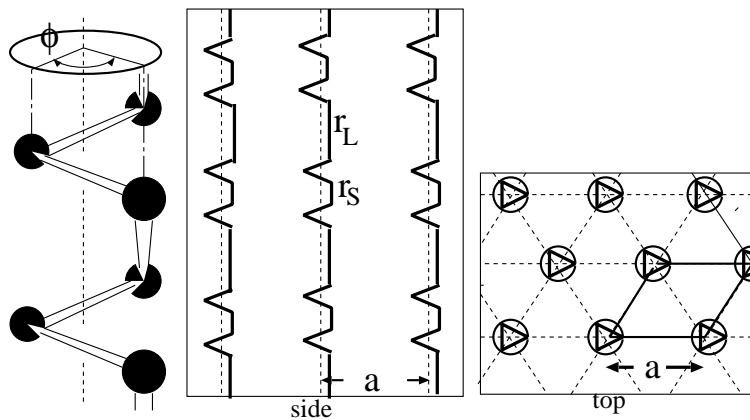


Fig. 1. Structural model. Figures in the center and on the right respectively represent the schematic situation when the model structure is viewed from the side and from the top. ϕ is the rotation angle, a and c are the lattice constants. Each solid line represents a bond.

We use the density functional method with local density approximation.^{13–15)} We calculate the total energy of the system by means of the steepest descent method. We employ the norm-conserving pseudopotential.¹⁶⁾ A simulation box with periodic boundary condition is taken as a primitive cell of a hexagonal lattice. The wave functions are expanded by the plane wave within the energy cutoff, 10 Ry.

Results and discussion

When P is increased at a constant T , the volume is decreased owing to the compression. By making use of the fact from the experimental results that the compression reduces the lattice constant a and keeps c fixed,⁷⁾ we calculate the band structures for various c/a or a/a_0 , where c is fixed to the experimental value and a_0 is the lattice constant of crystalline value. In order to express the degree of structural disorder, we use the ratio (r_L/r_S) between the lengths of a long and short bond.

In this section, we present the results concerning the band gaps of compressed Se and Te. We also give physical analyses of our results and compare the electronic properties between Se and Te.

Contour plots of E_g of Se and Te are shown in Figs. 2 (a) and (b), respectively.

First, we study the case of $r_L/r_S = 1.0$, in which the bond

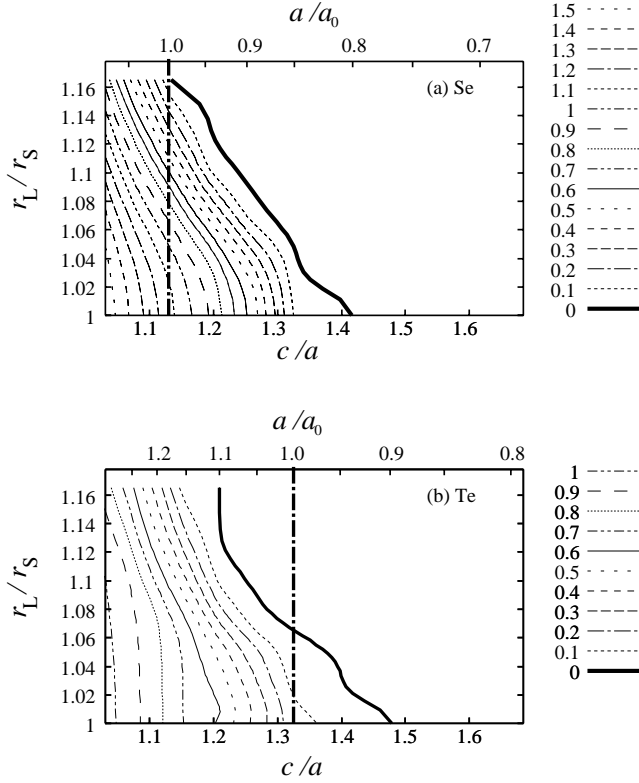


Fig. 2. Contour plots of energy gap (E_g) of (a) Se and (b) Te on c/a (a/a_0) and r_L/r_S plane. A dashed-and-dotted line shows c/a (a/a_0) under normal pressure, where a_0 is the lattice constant of the crystal.

lengths are the same for all bonds. When a is decreased in this case, that is, P is increased, we can see from Fig. 2 that the system transforms from a nonmetal to metal phase at $a/a_0 = 0.8$, or $c/a = 1.42$ for compressed Se and at $a/a_0 = 0.9$, or $c/a = 1.48$ for compressed Te. These nonmetal-to-metal transitions are caused by the increase of band widths when the interchain distance a is reduced. It should be noted that, at the nonmetal-to-metal points, the values of c/a are almost the same both for compressed Se and Te. These values are in quantitative agreement with the experimental results.⁷⁾

However, when $r_L/r_S > 1.0$, in which the system has structural disorder, a nonmetal-to-metal transition takes place at a/a_0 larger than that for the case of $r_L/r_S = 1.0$, which corresponds to a crystalline structure. The reason for this is explained as follows; the energy of anti-bonding levels corresponding to the long bonds reduces and accordingly E_g is decreased. The system transforms from a nonmetal to a metal phase under a lower pressure when the system has structural disorder.

Next, we compare the nonmetal-to-metal phases on a/a_0 (c/a) and r_L/r_S planes between Se and Te. When a/a_0 is decreased, the compressed Se transforms from a nonmetal to a metal phase at a lower value of a/a_0 than that of the compressed Te. This shows that the nonmetal-to-metal transition for Se under compression takes place at a pressure higher than that for Te.

When $a/a_0 = 1.0$, that is, the pressure is normal, Te transforms from a nonmetal to a metal phase at a value of r_L/r_S lower than that of Se. This result indicates that Te becomes metallic even when the degree of structural disorder is smaller than that of Se at the nonmetal-to-metal point. This situation accounts for that ℓ -Se under a normal pressure is a semiconductor, while ℓ -Te is a metal.

On the other hand, the values of c/a at the nonmetal-to-metal point are the same both for compressed Se and Te. The border lines of nonmetal-to-metal transformation scaled by c/a and r_L/r_S on Se and Te phase diagrams are almost the same with each other (Fig. 2). This results indicate that the pressure and temperature phase diagrams of Se and Te for nonmetal-to-metal transition are quantitatively similar to each other when the parameters are properly scaled.

Conclusions

We have constructed models for compressed Se and Te, and calculated their energy levels by the density functional method. Our results are summarized as follows.

- (1) When the volume is compressed under high pressure, the band width is increased and the system transforms from a nonmetal to a metal phase.
- (2) When the system has a structural disorder for the bond length, the energy of the anti-bonding bands, which correspond to the long bonds, is decreased. This result accounts for the reason why the nonmetal-to-metal transition in liquid Se takes place at a pressure lower than that for c -Se and the reason why the nonmetal-to-metal transition of Te takes place in melting from a crystal to a liquid.

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